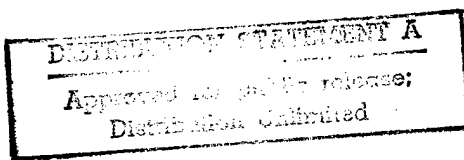*General Electric Co.*

INVESTIGATION OF GROUP IV-A
METAL VAPOR GENERATION AND FLUX BEHAVIOR

P. D. ZAVITSANOS

J. A. GOLDEN

FINAL REPORT

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The results of this work constitute a portion of a study investigating the potential of several Group IV-A metal oxides, such as SnO* for producing an electronic transition (visible) chemical laser via the oxidation of metal atoms by N_2O.

The vapor composition of Sn, Ge and Si was investigated by high temperature mass spectrometry up to temperatures where the respective vapor pressures

reached one torr or higher.

In the case Sn and Si, 95% and 90%, respectively of the vapor exists in the atomic form; the rest exists in the form of dimers, trimers, and tetramers. The germanium vapor consists of 98% atomic species and traces of Ge_2.

The reaction between titanium and boron was utilized to demonstrate the generation high density tin vapor.

Emission spectra of the Sn/N_2O system (where Sn was generated by RF heating and/or via the Ti/B reaction) suggest that the intensity of the green system SnO ($a\ ^3\Sigma$) is reduced with increasing density of tin vapor.

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I. INTRODUCTION

The gas phase reactions of certain Group IV-A metals with N_2O can give rise to electronically excited metal oxide species which have been considered candidates as active molecules for electronic transition chemical lasers. The objective of this program was to obtain experimental data on selected Group IV-A metals as it pertains to the properties of the gas phase generation and transfer and also devise practical schemes for developing a metal vapor generator which may permit an evaluation of their potential as laser pumping sources.

II. APPROACH

Metal atoms of Sn, Ge, and Si, were generated at densities as high as 10^{17} with induction RF heating. The metal vapor flux is characterized in terms of polymer and particulate formation (in the absence and presence of foreign gases) using mass spectrometry and other techniques. The addition of N_2, N_2O, A, and He were investigated.

In addition, intermetallic reaction schemes were evaluated for their potential of producing the required metal flows and a metal vapor generator was developed and tested.

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III. EXPERIMENTAL

1. Study of Metal Vapor Generated by RF-Induction Heating

RF heating and Knudsen effusion have been used extensively in high-temperature mass spectrometric work to generate and diagnose metal vapors and their oxidation products at temperatures as high as $3000^{\circ}K$[1,2,3].

The experimental arrangement is shown in Figures 1 and 2. Figure 1 shows the inductively heated Knudsen cell in-place in the Bendix Model 12 time-of-flight mass spectrometer. The water-cooled induction coil enters the furnace chamber from the bottom flange. The crucible and its holder are supported on three tantalum rods on the inlet assembly.

The Knudsen crucible dimensions are 0.6 cm I.D. x 1.2 cm deep with a 0.13 cm wall with a crucible cover, 0.32 cm thick x 0.9 cm (diameter), which has a 60° conical orifice whose minor diameter is 0.08 cm.

The temperature of the crucible is measured with a Leeds and Northrup optical pyrometer by sighting into the orifice (as shown in Figure 1). Corrections due to prism and window were made in all the reported temperature values.

The vapor generated in the crucible in chamber II, after traveling 2 cm through a vacuum of $P_{II} = 10^{-6}$ torr, enters chamber I (through a slit 0.5 cm x .05 cm) which is differentially pumped to a pressure $P_1 = 10^{-7}$ torr. The vapor travels 6 cm in chamber I before it reaches point G where an electron beam of controlled energy is directed perpendicular to the metal vapor beam.

The interaction with the pulsed electron beam produces positive ions which are in turn pulsed by ion grid H (-2.8 KV) and all receive an equal energy impulse. Since their respective velocities vary according to their mass to charge ratios (m/e) the ions are separated in bunches of equal m/e. As each bunch strikes the collector cathode, it is converted into an electron signal and through secondary electron emission in the electron multiplier is amplified. The resultant (amplified) electron pulses pass across a resistor and the resulting voltage pulses (after further amplification in the wide band amplifier) are displayed on an oscilloscope screen and compose the mass spectrum. (The lighter masses appear on the left of the screen.) The oscilloscope is triggered by a pulse whose timing relative to that of the ion focus pulse can be varied. Mass spectrometer positive ion signals can be also obtained by using the analog output. The analog unit integrates many single-sweep spectra which are detected by a gate. A single-sweep spectrum results from one cycle of operation at a rate of 10^4 per second. The gate sweeps the spectrum (at a slowly and linearly increasing time delay with respect to the ionization pulse) and represents the average of a number of ionization pulses at each mass peak. The data reported in this document were obtained by using the analog unit.

Modifications of the apparatus which allow the study of gas phase oxidation reactions of the metal atoms involve increasing the distance between the crucible and the entrance slit to the ion source and the introduction of the oxidant gas in the path of the metal atoms as discussed at a later section.

A - INDUCTION COIL
B - TANTALUM HEAT SHIELD
C - KNUDSEN CRUCIBLE AND LID
D - WATER COOLED PORTION OF
      CHAMBER
E - MOVABLE SHUTTER
F - TOF SOURCE ENTRANCE SLIT

G⁻ - IONIZING ELECTRON BEAM
H - ION GRID
 I - VIEWING WINDOW ON MULTIWINDOW
      ASSEMBLY
J - PRISM
K - OPTICAL PYROMETER

TOF SOURCE
HOUSING

FIELD FREE FLIGHT TUBE

TO MULTIPLIER

IONS
TO PUMP(I)

P_I

P_{II}

TO PUMP(II)

TO SCOPE
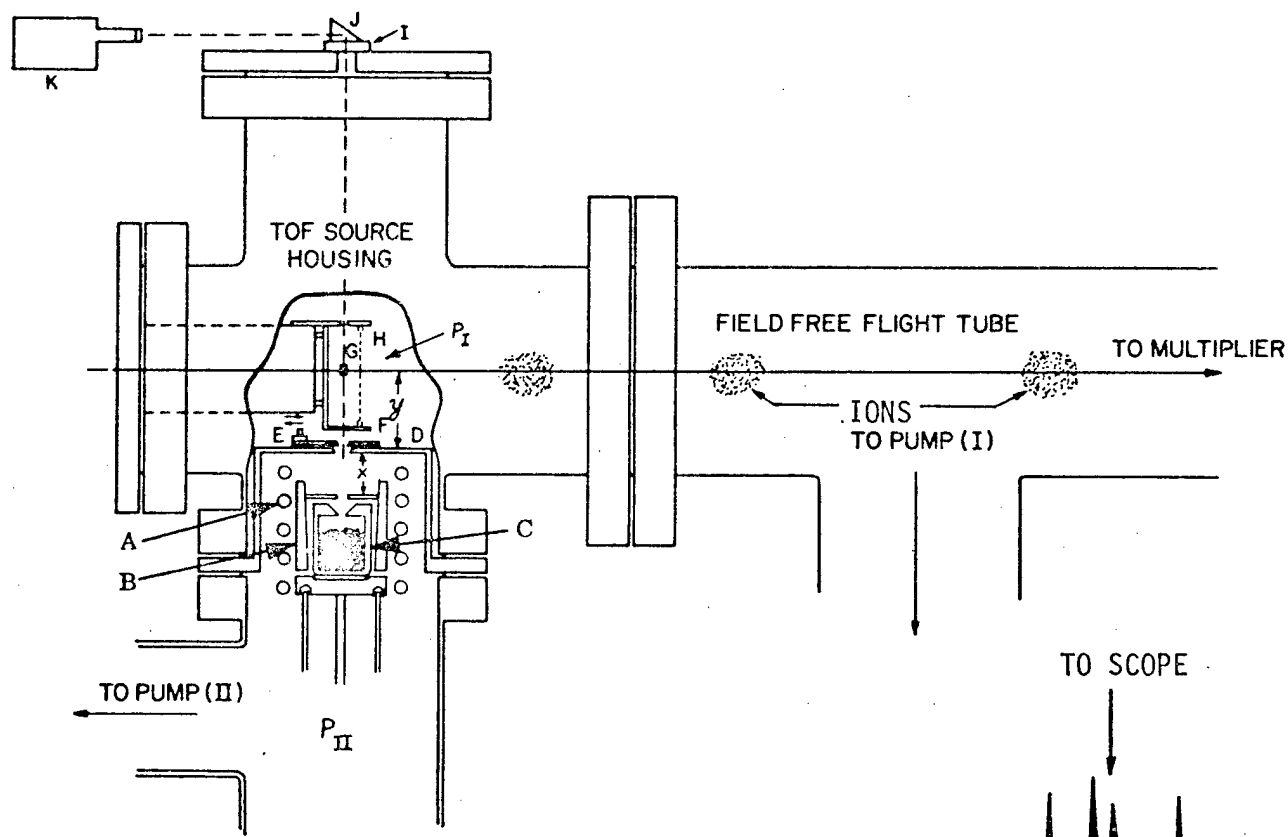
FIGURE 1.   KNUDSEN CRUCIBLE MASS SPECTROMETER APPARATUS

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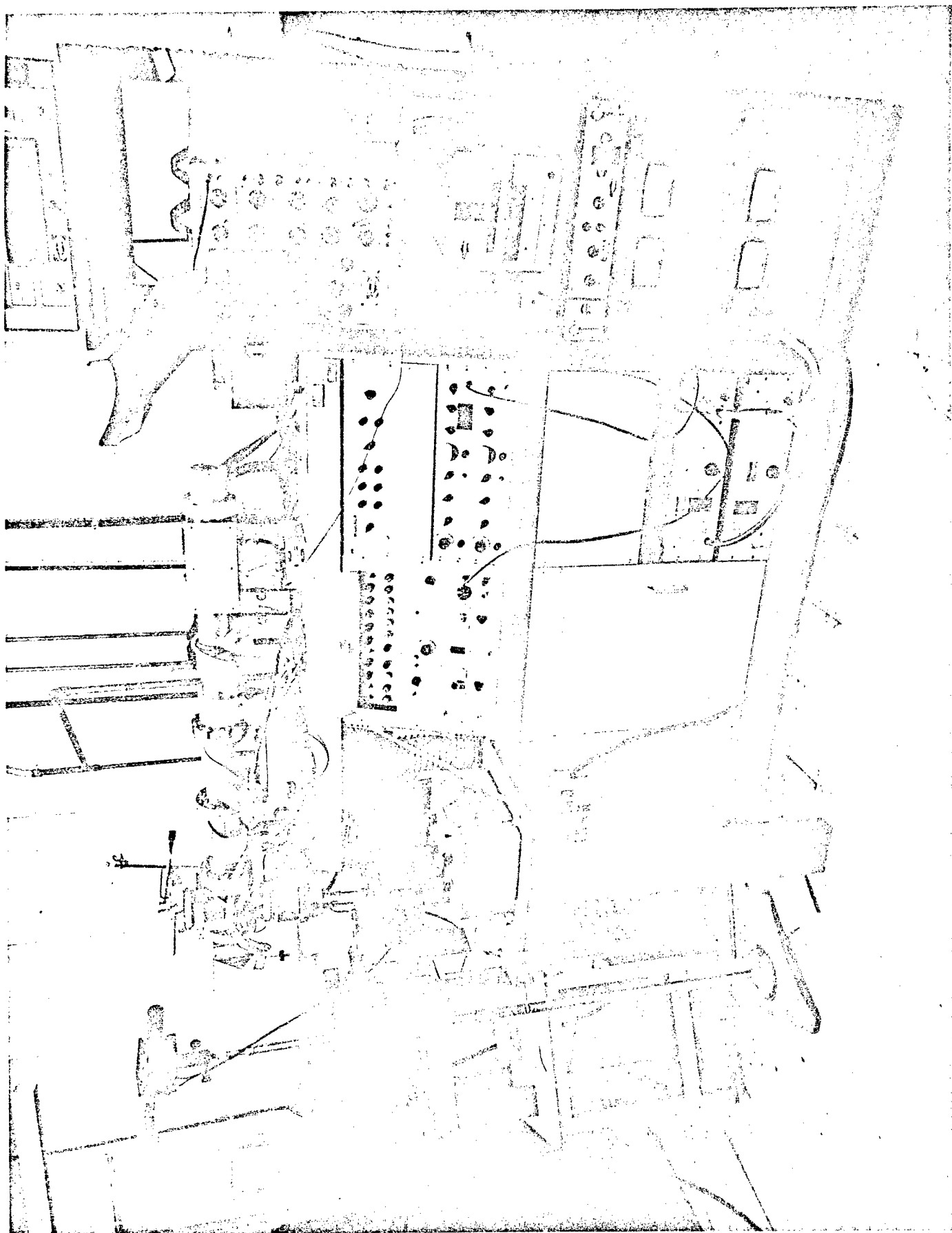
FIGURE 2. INDUCTIVELY HEATED FURNACE IN TIME-OF-FLIGHT MASS SPECTROMETER

a. <u>The Composition of Tin and Tin Oxide Vapors</u>

Data were obtained on the composition of tin vapor in the temperature range $1500^{\circ}K - 2073^{\circ}K$. The data were analyzed in order to obtain information on the relative significance of all the species existing in the vapor under high concentration conditions. Typical spectra of Sn, Sn_2, and Sn_3 are shown in Figure 3. It is apparent that all seven isotopes of the tin monomer (Sn) are resolved and in terms of mass ion intensity match very well the expected isotopic abundance, i.e.,

$$Sn^{116} = 14.3\%, \ Sn^{117} = 7.6\%, \ Sn^{118} = 24\%, \ Sn^{119} = 8.6\%,$$

$$Sn^{120} = 32.85\%, \ Sn^{122} = 4.9\%, \ and \ Sn^{124} = 5.9\%.$$

In addition, the dimer, trimer, and tetramer were also observed. However, due to the many combinations of isotopes, the number of peaks increases in the formation of polymeric species and it is for this reason that resolution of the individual peaks is difficult.

Adjustments for this effect were made by measuring the highest mass peak and multiplying it by a corresponding correction factor to account for all the isotope combinations.

The partial vapor pressures of Sn_2, Sn_3, and Sn_4 were computed relative to the monomer from the relationship:

$$P \ Sn_x = P \ Sn \ \dot{x} \ I \ Sn_x / I \ Sn \ \dot{x} \ \sigma_1 / \ \sigma_x \ \dot{x} \ C_i$$
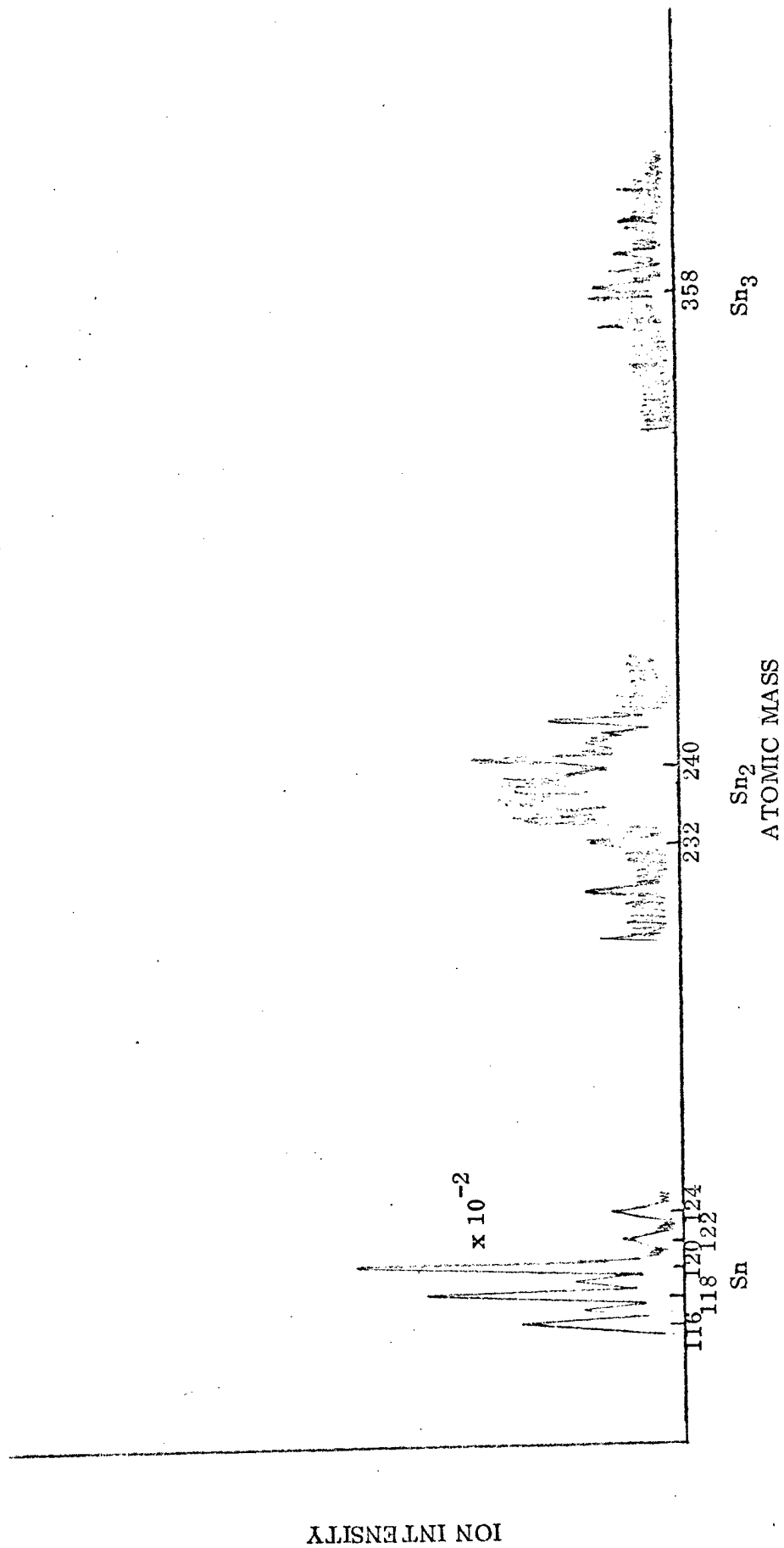
FIGURE 3. TIN VAPOR MASS SPECTRUM

where

P = Vapor Pressure

I = Ion Intensity

σ = Ionization Cross Section (Relative)

C_i = Correction Factor for Isotopes

Mass spectrometry data on relative ion intensities as well as calculated ratios of vapor pressures are shown in Table I. The computed partial vapor pressures of Sn_x (x = 2, 3, 4) are shown in Figure 4. It is apparent from these data that even at the highest temperature of the measurements the contribution of the polymeric species is minor. The composition of the vapor at 2000°K where the total tin pressure is about 2 torr only 5% of the total weight is in a form other than atomic. The relative contributions of Sn_2, Sn_3, and Sn_4 are 3%, 2%, and 0.2% respectively, as shown in Table II.

In order to predict the condensation characteristics of tin oxide(s), tin oxide vapor species in equilibrium with the condensed phase of Sn/SnO_2 mixtures were investigated mass spectrometrically in the temperature range of 1223°K - 1323°K. The resulting vapor consists of SnO, Sn_2O_2, and Sn_3O_3 species in quantities shown in Figure 4. The total vapor pressure of the oxides in this temperature range in comparison to tin vapor is two orders of magnitude higher.

TABLE I

THE COMPOSITION OF TIN VAPOR

T°K	$\dfrac{10^3}{T°K}$	I Sn	I Sn$_2$	$\dfrac{I\,Sn}{I\,Sn_2}$	$\dfrac{P\,Sn_2}{P\,Sn}$	I Sn$_3$	$\dfrac{I\,Sn}{I\,Sn_3}$	$\dfrac{P\,Sn_3}{P\,Sn}$	I Sn$_4$	$\dfrac{I\,Sn}{I\,Sn_4}$	$\dfrac{P\,Sn_4}{P\,Sn}$
1783	0.56	40,200	297	135.4	$10^{-2.13}$	19	2116	$10^{-3.2}$	6	6,700	$10^{-3.3}$
2073	0.48	68,500	883	77.6	$10^{-1.89}$	285	240.3	$10^{-2.25}$	9	7,611	$10^{-3.36}$
2003	0.499	7610	191	39.8	$10^{-1.6}$	38	200.2	$10^{-2.14}$	2.0	3,805	$10^{-3.06}$
1723	0.58	5200	48	108.3	10^{-2}	14	371.4	$10^{-2.44}$	1.6	3,250	$10^{-2.993}$

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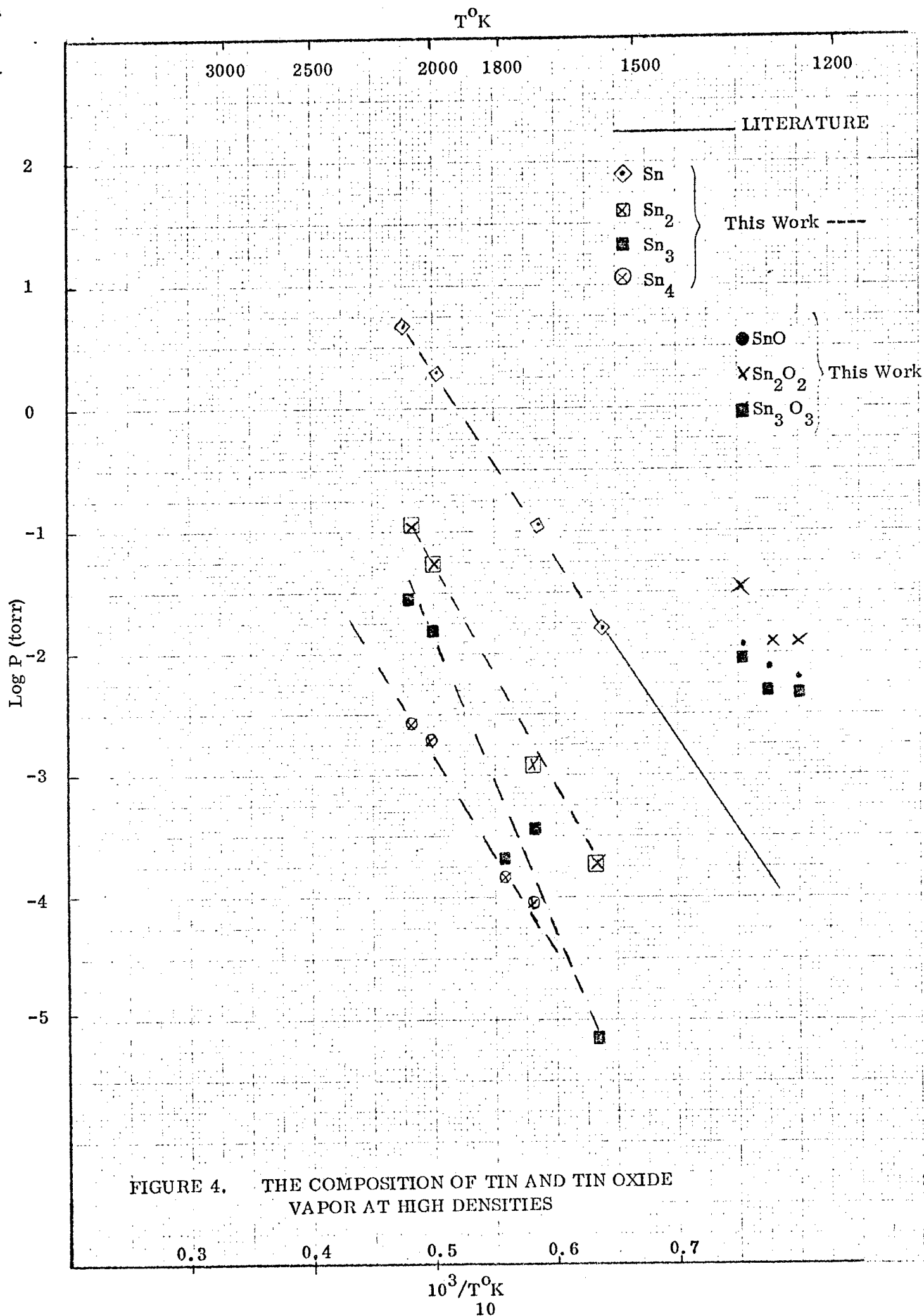
FIGURE 4.   THE COMPOSITION OF TIN AND TIN OXIDE
VAPOR AT HIGH DENSITIES

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TABLE II

COMPOSITION OF TIN VAPOR AT 2000°K

$$P_{TOTAL} = 2 \text{ TORR}$$

$$\frac{P \, Sn_2}{P \, Sn_1} = 1.7 \times 10^{-2}$$

$$\frac{P \, Sn_3}{P \, Sn_1} = 6.7 \times 10^{-3}$$

$$\frac{P \, Sn_4}{P \, Sn_1} = 5.5 \times 10^{-4}$$

$\therefore$ ~95% OF Sn ATOMS EXIST AS Sn

3% OF Sn ATOMS EXIST AS Sn_2

2% OF Sn ATOMS EXIST AS Sn_3

.2% OF Sn ATOMS EXIST AS Sn_4

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b. <u>The Composition of Germanium Vapor</u>

After realizing that tantalum was not a suitable container for liquid germanium, a tungsten crucible was used for this study. The data obtained in the temperature range $1700^{\circ}K$ - $1865^{\circ}K$ on the germanium system are shown in the attached Figure 5. The dimer $Ge_2(g)$ was observed at $1865^{\circ}K$ for the first time and it appears to correspond to less than 2% (by weight) of the total vapor. No higher polymers were observed.

c. <u>The Composition of Silicon Vapor</u>

The vaporization of elemental silicon was also investigated by the use of induction heating and Knudsen effusion mass spectrometry. Measurements were made on the composition of the vapor in the temperature range $1660^{\circ}K$ - $2380^{\circ}K$. These data as shown in Figure 6 show the existence of the dimer, trimer and tetramer which collectively account for approximately 10% of the total vapor.

d. <u>Metal/Oxidizer Reaction System</u>

A system (shown in Figure 7) was assembled to examine the oxidation species of metal atoms generated by a sample contained in an RF (25 KW, 450 KHz) heated tantalum crucible. The reaction vessel is a pyrex cylinder (15 cm I. D. x 45 cm) which has two 5 cm diameter quartz windows located 22.5 cm from either end for optical measurements. At one end of the cylinder a metal plate is attached. The RF power transmission leads terminate in a copper coil (1/4" tubing) mounted on the plate. Metal samples are vaporized from a tantalum crucible (9 mm I. D. x 15 mm) mounted inside
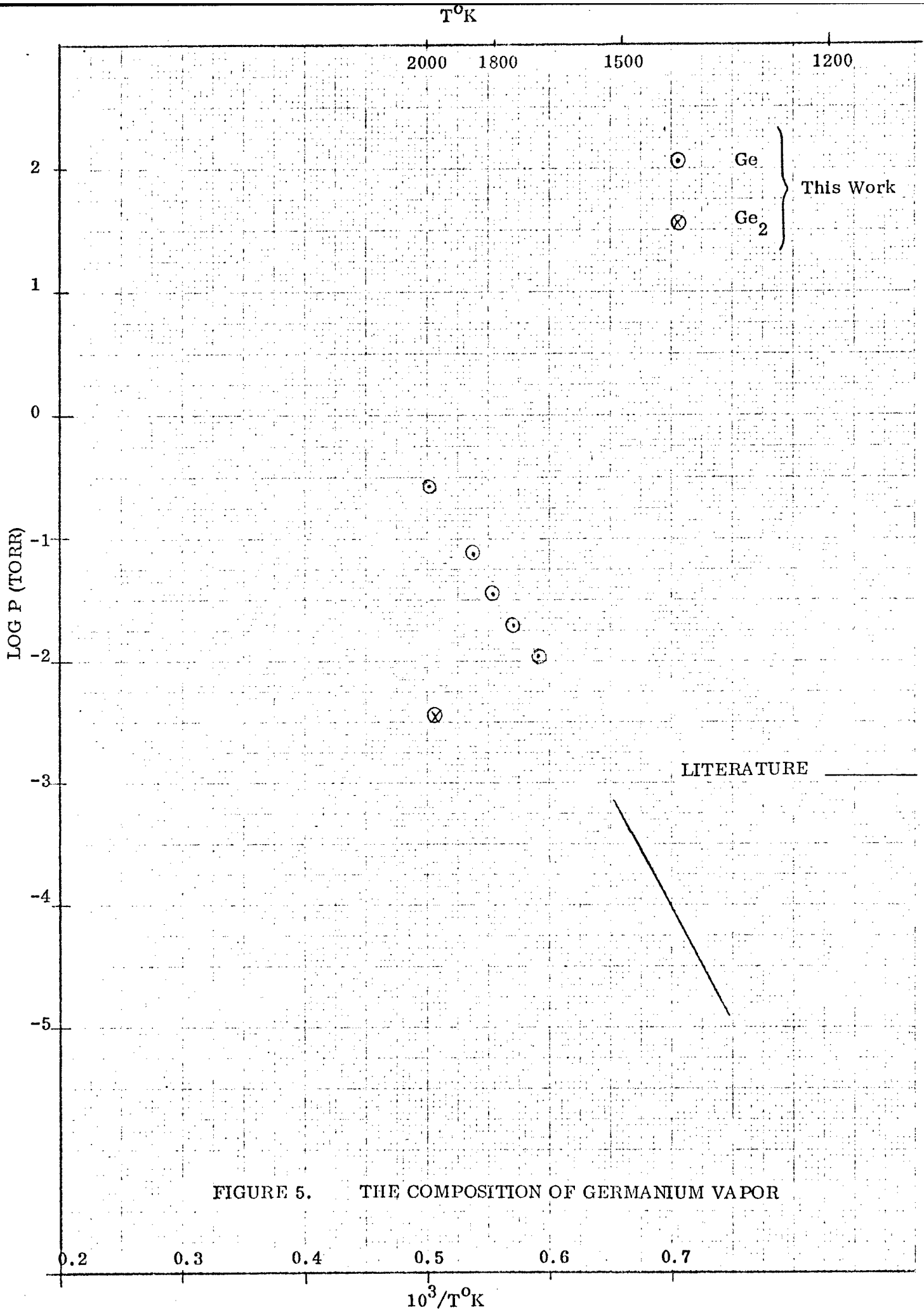
FIGURE 5.   THE COMPOSITION OF GERMANIUM VAPOR

FIGURE 6. THE COMPOSITION OF SILICON VAPOR

ION SOURCE CHAMBER

GAS SAMPLING
VALVE ASS'Y

VACUUM PUMP

PYREX PIPE
15 cm I. D. x 45 cm

QUARTZ WINDOWS
5 cm Dia.

RF COUPLING COIL

KNUDSEN CRUCIBLE
(9 mm I. D. x 15 mm)
CONTAINING METAL
SAMPLE

MOVABLE TUBE

CARRIER GAS INLET
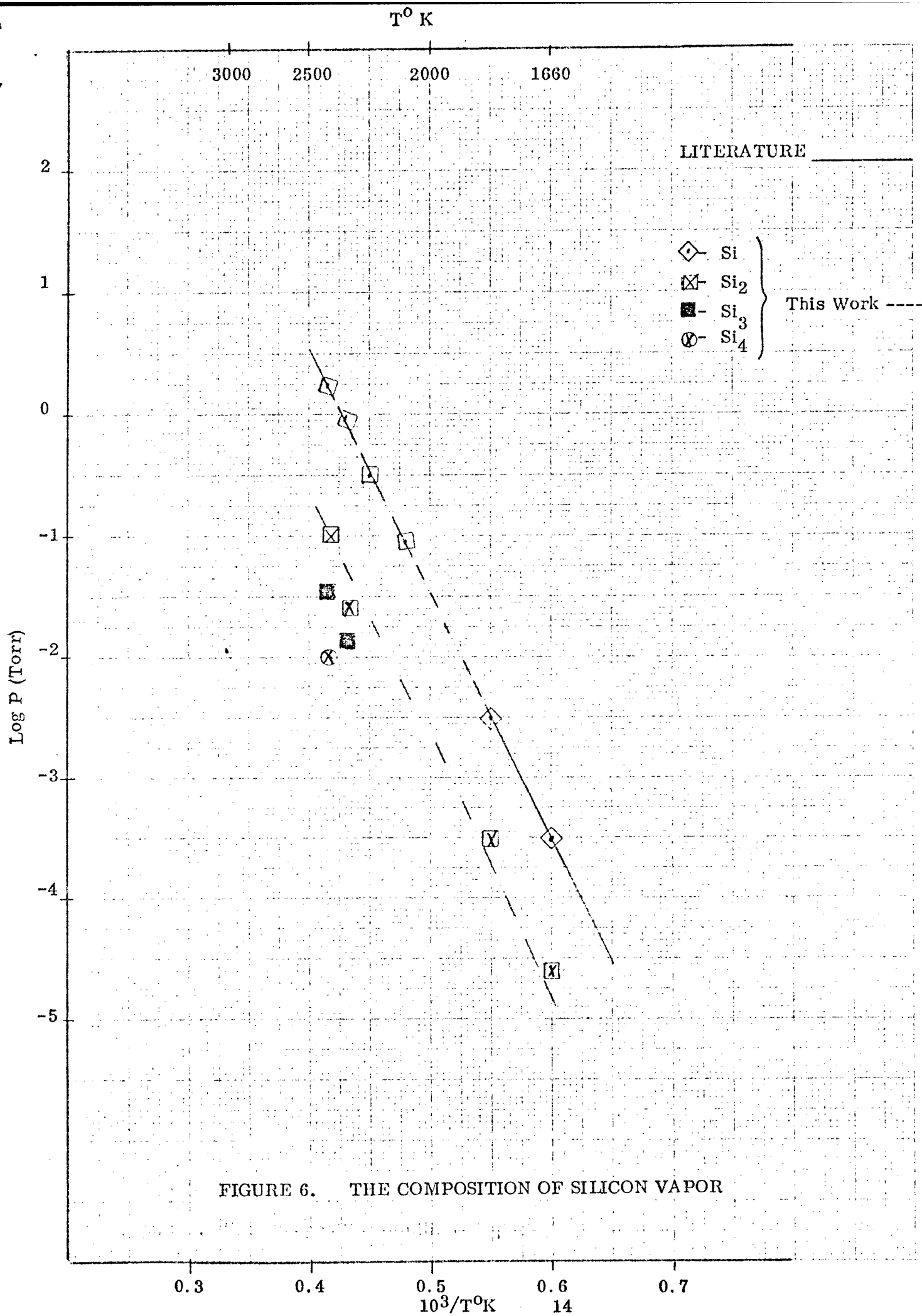
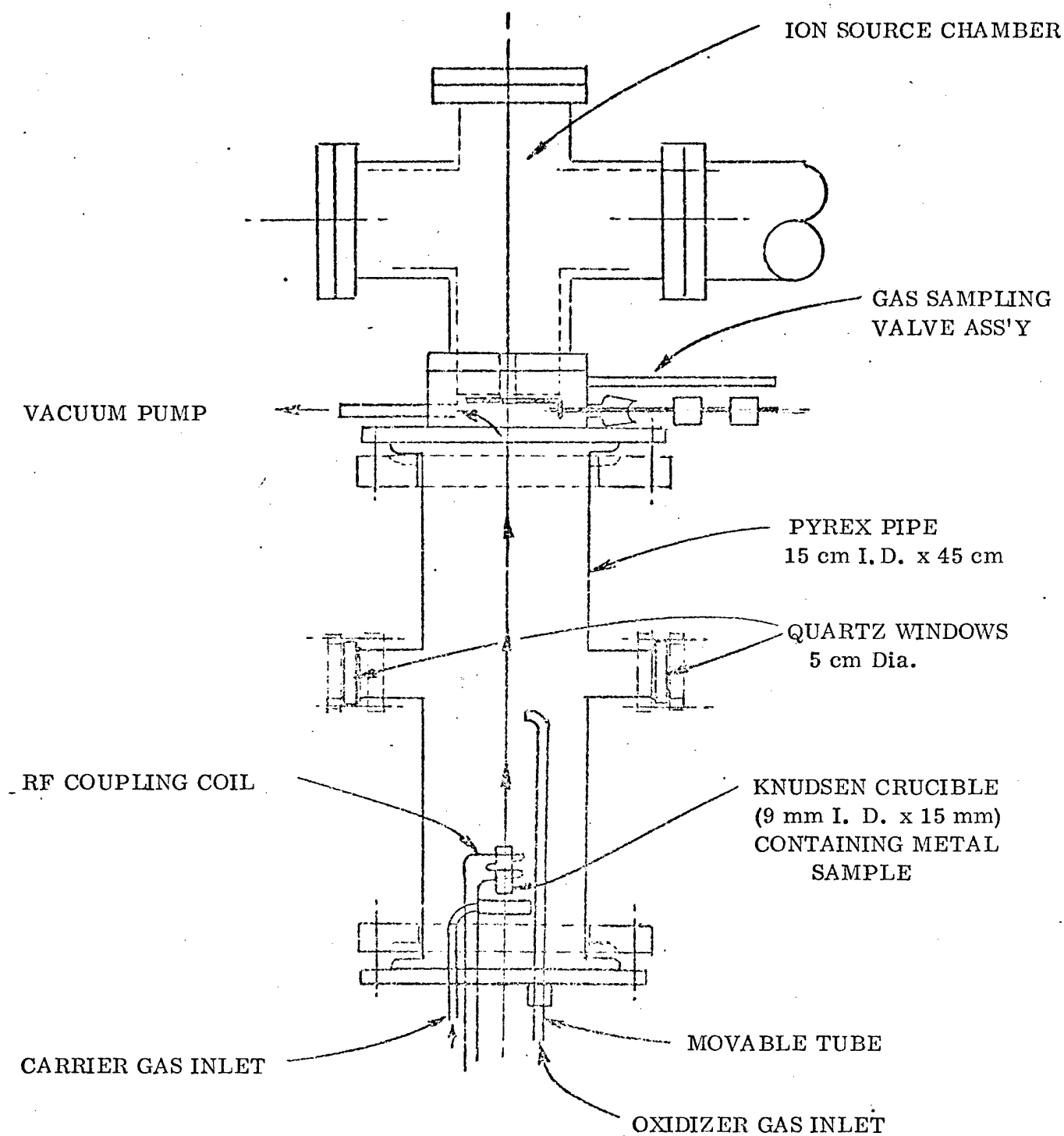OXIDIZER GAS INLET

FIGURE 7.   METAL VAPOR OXIDATION SYSTEM

the coil as shown in Figure 7 . The plate also has two gas inlet tubes

and a thermocouple feed thru. One gas inlet is used to pass an inert

carrier gas past the heated curcible and thereby transport the metal

vapor along the cylinder where reaction with oxidizer gas occurs.

The second gas inlet tube supplies oxidizer gas flow. This tube is

movable along the cylinder in order to vary the extent of oxidation of

the metal vapor passing the optical windows. In addition, the vapori-

zation temperature, the inert gas/oxidizer pressure, and the gas vel-

ocities are adjustable parameters.

The pyrex cylinder is attached to the high pressure side of a solenoid

operated gas sampling valve, the low pressure side of this valve is mounted

on the mass spectrometer flight tube near the ion source chamber. This was to

allow the metal/oxidizer stream to be sampled for species analysis.

Several experiments were performed using tinshot samples RF heated

to $1773^{O}K$ – $2073^{O}K$ in a tantalum crucible. The crucible was heated in

flowing argon carrier gas with and without N_2O flow through the oxidizer

gas inlet. The argon pressure was 10 torr and the N_2O was 2 torr. With

the crucible at $1600^{O}C$ and with both Ar and N_2O flowing a blue disc shape

flame ($\sim$1 cm diameter x 1 cm high) was observed above the crucible.

The mass spectrum of the products above this flame was recorded using

the high pressure gas sampling valve. The spectrum showed argon and

N_2O mass peaks but no tin or tin oxides were observed. Spectra obtained

without the N_2O oxidizer also showed no Sn mass peak.

Since there was no Sn mass signal without oxidizer in the gas flowing past the crucible, work was directed toward increasing the Sn metal concentration at the sampling valve pin hole. This was done by increasing the carrier gas velocity and by operating the crucible in the $2273^{\circ}K - 2473^{\circ}K$ range where the vapor pressure of tin is about ten times higher than the previous range. Tin was vaporized in this temperature range in flowing argon at pressures from .3 to 20 torr. There was no tin or tin oxide mass signal when these metal vapor/gas systems were sampled with the pinhole-slide sampling valve. The argon and N_2O mass peaks were readily detected. This work was done with the crucible located 27 cm from the mass spectrometer entrance slit.

In a further attempt to record tin and tin oxide mass peaks, several changes were made in the system: (1) crucible-slit distance was reduced to 18 cm, (2) the sampling valve pinhole diameter was increased from 250 to 750 microns, (3) the gas sampling time was increased from .1 to .5 seconds. A series of vaporization experiments at temperatures up to $2273^{\circ}K$ again showed no tin or tin oxide mass signals yet substantial amounts of tin was vaporized from the crucible in the process. It was thus concluded that serious condensation phenomena were taking place which prevented the transfer of atomic and molecular species into the ion source of the mass spectrometer and therefore no further work was done with this system.

2. Use of Intermetallic Reactions for Tin Vapor Generation

The availability of high density metal vapor has been considered a requirement in the development of chemically pumped laser candidate systems. Thus a portion of this study was directed towards the study of intermetallic reactions as a means of producing high density tin. Specifically, the highly exothermic reaction leading to the formation of titanium diboride has been considered:

$$Ti\ (s)\ +\ 2B\ (s) \longrightarrow Ti\ B_2(s)\ +\ \triangle\ H$$
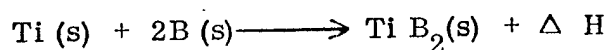
The exothermicity ($\triangle$ H) of this reaction is about 1.2 kcal/gm and can raise the temperature of the product Ti B_2 to temperatures far in excess of the boiling points of the group IV-A elements (with the exception of carbon.

The thermochemical evaluation of the Ti/B/Sn system is shown in Table III where the heat released in the formation of TiB_2 can be compared to the enthalpy change of the mixture during the heating cycle and the subsequent vaporization of tin.

In providing theoretical estimates for generating tin vapor, it was assumed that the mixture is first heated to the boiling point of tin (2960°K) and at that point the excess energy is consumed in vaporizing tin:

Heat of Formation of TiB_2 = Total Enthalpy Change + Heat Consumed in Sn Vaporization

or $\triangle H_f\ (Ti\ B_2)\ =\ (H^{\circ}_{2960} - H_{298})\ Ti\ B_2$

$+\ n\ (H^{\circ}_{2960} - H^{\circ}_{298})_{Sn}\ +\ n/(\triangle H^{\circ}_{vap})Sn$

where n = no. of moles of Sn vaporized or 84.7 = 57 + n (20.6 + 69.4),

therefore, n = 0.3.

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TABLE III. THERMOCHEMICAL PROPERTIES OF THE Ti/B/Sn SYSTEM[8] [9]

Material	Melting		Enthalpy Change	Heat of Formation	Vaporization	
	M.P. $^{\circ}K$	ΔH (k cal/mole)	$H_{2960} - H_{298}$ (k cal/mole)	$\Delta H_{f(2960)}$ (k cal/mole)	B.P. $^{\circ}K$	ΔH (b.p.) (k cal/mole)
Sn	505	1.7	20.6		2960	69.4
Ti	1940	4.0	15		3575	102
B	2300	5.1	17		4200	129.2-137.9
$Ti\,B_2$	3193	12 ± 3	57	-84.7	> 4000	

It would appear then that the formation of one mole of TiB_2 can theoretically generate 0.3 moles of Sn. This suggests that the desired stoichiometry should be:

$$Ti + 2B + 0.3 \text{ (or less) Sn}$$

$$Ti\ B_2 \text{ (c)} + .3\ Sn \text{ (g)}$$
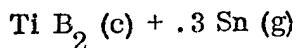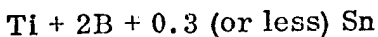
which represents 33.7% Sn (or less) in terms of total mixture weight.

a. Yield Measurements - Open Tube Configuration

Several runs were carried with Ti, B mixtures at molar ratios of one to two, respectively. Tin was added at 5, 10, 15, and 20% of the total weight. The mixture was placed in cylindrical crucible made out of ZrO_2 of 3 cm in I. D. and fired with a tungsten (hot) wire. The first few runs were carried out inside a quartz in flowing argon at one atmosphere. In every case, the initiation was successful and resulted into tin vapor deposits onto the inner walls of the quartz tube.

The amount of tin vaporized was obtained by chemical analysis of the residue after the firing: The total residue was taken and ground to a powder; it was then thoroughly mixed, and a representative sample was taken from the total. The sample was then digested with 30% HNO_3 until all reaction had ceased. Subsequent addition of concentrated HC1 assures that all tin is in solution. After 2 hours of treatment with HC1, the samples were filtered and diluted in 100 ml volumetric flasks.

The analyses of the solutions were carried by atomic emission spectroscopy using appropriate calibration standards as shown in Figure 8 .

FIGURE 8. TIN ANALYSIS BY FLAME EMISSION SPECTROSCOPY

WAVELENGTH – 284 nm

FLAME–NITROUS OXIDE/ACETYLENE

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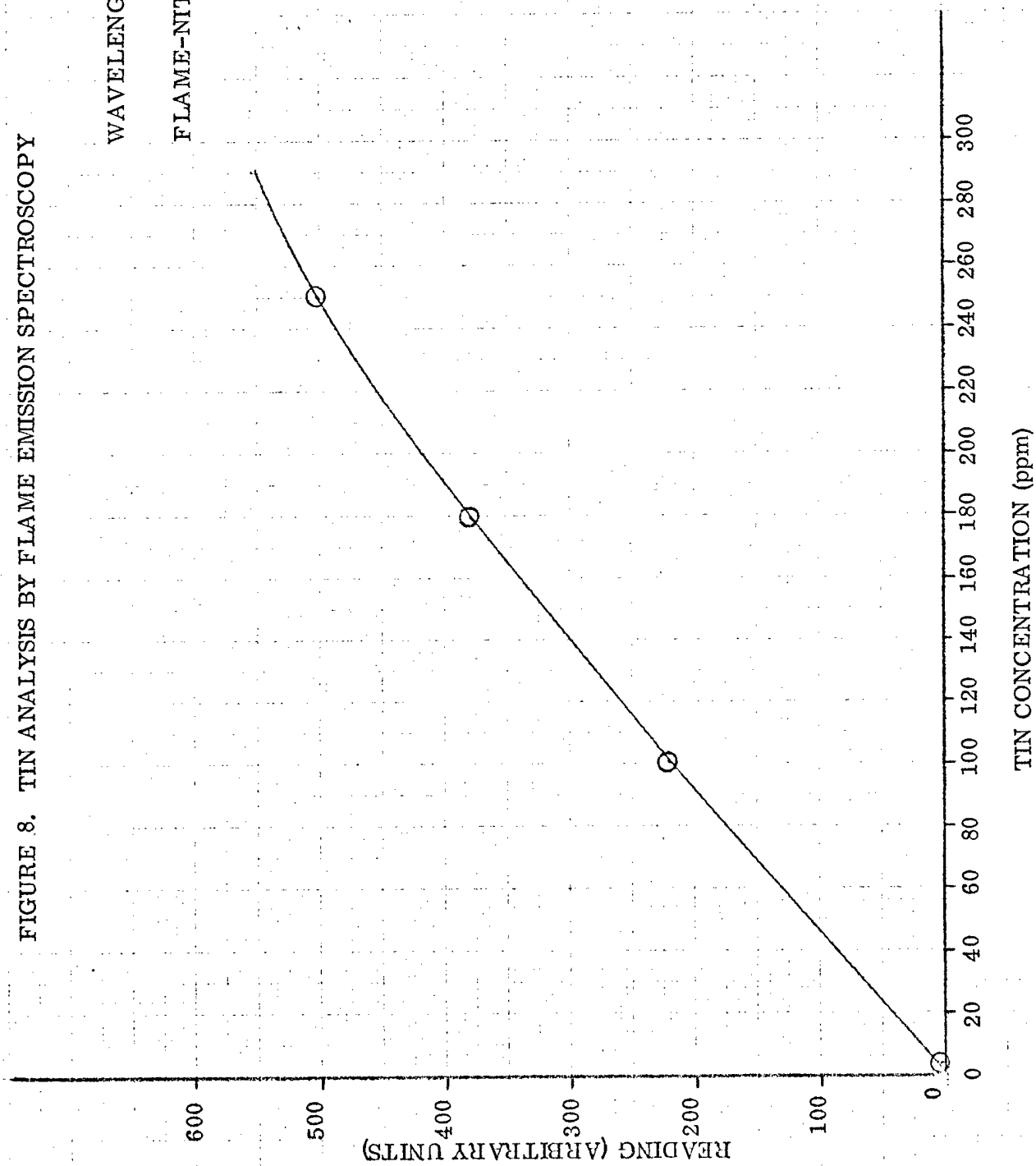
Five such runs have been analyzed. The results as shown in Table IV suggest that as expected the amount of tin vapor produced depends not only on the amount of tin added but also on the geometry of the generator. Open ZrO_2 containers vaporized 40-60% of the available tin (Runs 3, 4, and 5), while the presence of an orifice may constrict the flow and reduce the vapor yield considerably (Run 2).

b. <u>Yield Measurements - Slotted Tube Configuration</u>

The open tube reactor was modified in a way so that the vapor would be allowed to exit easily from a slotted configuration as compared to the point source. The tested design is shown in Figures 9 and 10 where the reactor consists of a slotted graphite tube. This configuration holds 3-4 gms of mixture and theoretically can produce up to 1 gm of Sn vapor.

In an effort to check our analytical technique, several runs were made on mixtures which were not fired or fired in a closed tube. Under those circumstances, it was possible to account for all added tin. When the mixtures were fired in the slotted tube, however, the residual tin was always lower than the introduced quantity.

The results of this series of experiments as shown in Table V suggest that in this configuration 30-50% of the available tin is removed from the residue and assumed to convert into the vapor state. In fact, after each experiment the inside surface of the vessel housing the generator is coated with shiny films of tin (not droplets). Subsequent analysis of the material coating the vessel showed that the observed deposits are elemental tin and as much as 50% of the missing tin (from the residue) may be recovered by this technique.

TABLE IV

TIN ANALYSIS IN TiB$_2$-Sn MIXTURES

RUN #	SAMPLE WT (gm)	% Sn-BEFORE	% Sn-AFTER	% Sn-REMOVED
1*	50.14	5	2.06	2.94
2*	49.95	10	7.43	2.57
3**	49.50	10	4.01	5.99
4**	49.70	15	8.28	6.72
5**	49.47	20	10.09	9.91

* CAP WITH 0.3 CM NOZZLE ORIFICE WAS PLACED ON ZrO$_2$ CRUCIBLE

** CAP WAS REMOVED
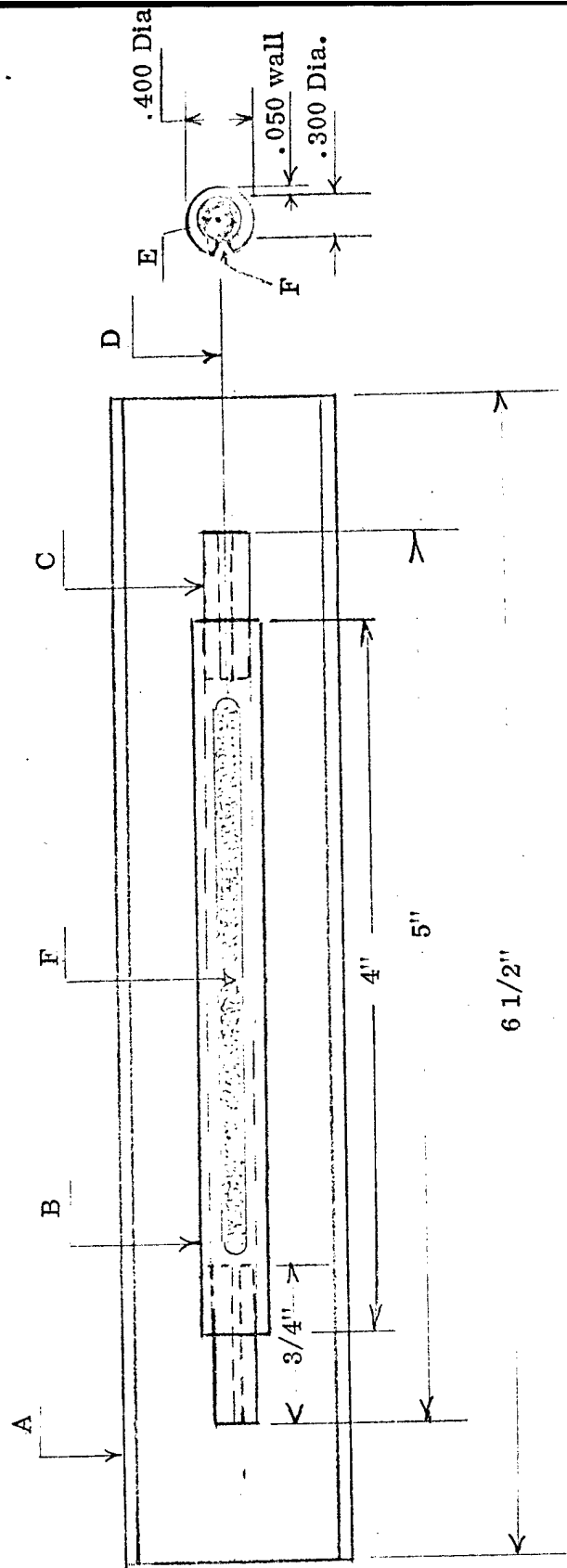
A – QUARTS TUBE .040" WALL – .9375" DIAMETER

B – GRAPHITE TUBE

C – GRAPHITE PLUG   2 EA.

D – .015 DIAMETER TUNGSTEN WIRE

E – Ti, B, Sn MIXTURE

F – TUBE OPENING, .015" WIDTH, 3.25" LENGTH

FIGURE 9.   TIN VAPOR GENERATOR

24
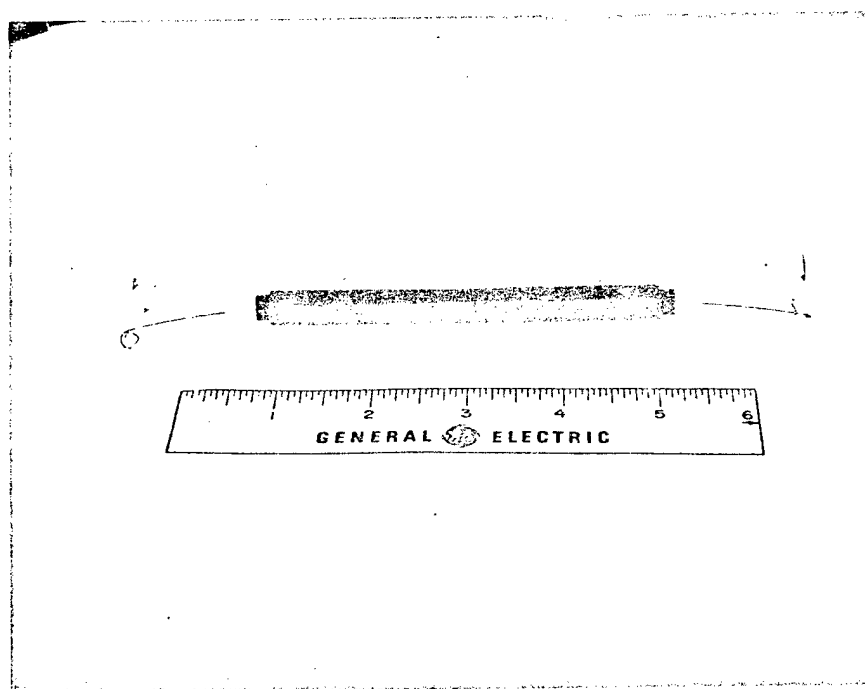
FIGURE 10. TIN VAPOR GENERATOR

TABLE V. TIN ANALYSIS IN THE Ti/B/Sn SYSTEM

RUN #	SAMPLE WEIGHT (gm)	% Sn BEFORE	% Sn AFTER	% Sn REMOVED	Sn-REMOVED (% OF THEORETICAL)
6 (Not Fired)	3.5	20	20	0	
7 (Fired in Closed System)	3.5	20	20	0	0
8 (Fired in Slotted Reactor)	3.15	4.76	1.87	2.89	60.7
9 "	3.3	9.1	4.84	4.25	46.7
10 "	3.45	13	6.9	6.1	46.9
11 "	3.6	16.7	10.85	5.85	35
12 "	3.1	4.76	3.58	1.18	24.8
13 "	3.3	9.1	3.91	5.19	57
14 "	3.5	13	7.5	5.5	42.3
15 "	3.6	16.7	11.1	5.6	33.5
					43.4 AVE.

3. Emission Spectra of Sn - N_2O System

Spectra were taken of the plume radiation from Sn vapor reacting with N_2O gas. The spectra were taken using a 1.5 meter (Bausch & Lomb) Grating Spectrograph equipped with a cylindrical condensing lens. The lens-spectrograph entrance slit orientation was adjusted to record the radiation from a line image located at the center of the tantalum crucible from the top edge upward to a point 5 cm above the crucible. Spectra were recorded on Kodak Tri-X film using a 60 micron spectrograph entrance slit. The exposure was integrated over the entire run in each series of experiments. i.e., .2 - .5 seconds for the Ti-B series and 2-3 minutes for the RF heated series. First and second order spectra were recorded covering the following wavelength range: $3600 \overset{o}{A}$ – $7200 \overset{o}{A}$ first order and $1950 \overset{o}{A}$ – $3600 \overset{o}{A}$ second order. Table VI gives a listing of the Sn and SnO species identified. Two series of experiments were run.

In the first series, a stoichiometric mixture of Ti & B powder (1.5g) was mixed with 50% Sn powder (by weight). Samples were contained in a tantalum crucible which had a slotted lid (1.5 x 14 mm slot) and fired using a hot nichrome wire. Experiments were run in a vacuum tank in which N_2O flowed through a small diameter metal tube located 2 cm above the crucible. Runs were made at 10 and 20 torr N_2O; the plumes produced were 10-12 cm wide and extended from 1-2 cm below the N_2O inlet to 10-12 cm above. These were intense flashes which had yellow, green,

and blue color. The spectrum of the lower 5 cm at the center of these plumes showed 6 bands of the SnO blue system (D $\longrightarrow$ X).

In the second series of experiments, high purity tin shot was vaporized using a 25 KW 450 KHz induction heater coupled by way of a copper coil to the tantalum crucible. Runs were made with a crucible covered with a slotted lid (1.5 mm x 14 mm) as well as with an open crucible. N_2O pressure was varied from .5 torr to 10 torr and the temperature range as 1373°K - 2373°K. The slotted lid runs produced a blue disc shaped plume 2-3 mm above the crucible. The disc was 3-4 cm diameter and 1-1.5 cm thick. It was brightest at 2 mm N_2O pressure and 1873°K - 2073°K crucible temperature. Spectra taken at 2 - 3 minutes exposure time showed the SnO blue D $\longrightarrow$ X and C $\longrightarrow$ X systems. The most sensitive Sn lines (2840° Å and 2863 Å) were weak on the film probably due to self absorption in the high density Sn vapor. However, two upper state Sn lines 3801 Å and 4525 Å appeared at an intensity level judged to be 50 - 100 times that of the sensitive Sn lines. This suggests that the Sn-N_2O system is producing a non-thermal energy distribution of Sn.

Several runs were made with an open tantalum crucible. A pale green fringe was seen at the top of the blue disc plume at 1573°K - 1673°K and 2 torr N_2O. With increasing temperature and/or N_2O pressure, the green disappeared. Spectra taken during these runs showed strong SnO blue (D' $\longrightarrow$ X and C $\longrightarrow$ X) and weak SnO green (a $\longrightarrow$ X) bands. The Sn 2840 Å, 2853 Å lines were weak while the 3801 Å and 4525 Å lines were medium intensity.

TABLE VI

EMISSION SPECTRA OF THE Sn-N$_2$O SYSTEM

A.   Sn O

System	Band Heads Wavelength ($\overset{o}{A}$)	V'	V''	Experimental Conditions		
D'$\Pi \rightleftharpoons$X' Σ^+ (A) Reference 4	3691.4	0	3	*	+	0
	3802.7	0	4	*	+	0
	3721.2	1	4	*	+	0
	3752.3	2	5	*	+	0
	3899.3	3	7	*	+	0
	3864.8	2	6	*	+	0
C $\rightleftharpoons$ X' Σ^+ Reference 5	3703.2	3	0		+	0
	3779.9	2	0		+	0
	3863.5	1	0		+	0
	3948.5	0	0		+	0
	3978.8	4	3		+	0
	4026.9	2	2		+	0
	4079.9	0	1		+	0
	4121.9	1	2		+	0
	4218.8	0	2			0
	4262.3	1	3			0
	4302.2	2	4			0
	4411.6	1	4			0
	4452.5	2	5			0
	4499.1	3	6			0
a$^3\Sigma^+ \rightarrow$X'Σ^+ Reference 6	5788.4	0	2			0
	5535.4	0	1			0
	5371.5	5	3			0
	5300.0					0
	6064.5	0	3			0

TABLE VI (Cont)

B. Sn Lines
(Reference 7)

Wavelength ($\overset{o}{A}$)	Term			
	Lower	Upper		
2863.3	$5P^2\ ^3P_0$	$-\ 6S\ ^3P^o_1$	+	0
2840.0	$5P^2\ ^3P_2$	$-\ 6S\ ^3P^o_2$	+	0
3801.0	$5P^2\ ^1D_2$	$-\ 6P\ ^3P^o_1$	+	0
4524.7	$5P^2\ ^1S_0$	$-\ 6S\ ^1P^o_1$	+	0

$*$ = Ti-B seeded with 50% Sn

$+$ = RF heated Sn (Slotted lid)

0 = RF heated Sn no lid

IV. CONCLUSIONS

Based on results gathered in the course of this study, the following conclusions can be made:

1. Based on mass spectrometric studies, the composition of tin vapor in the temperature range $1500^{\circ}K - 2073^{\circ}K$ consists mainly of tin atoms (Sn) and small quantities of dimers (Sn_2), trimers (Sn_3) and tetramers (Sn_4), totalling to less than 5% of the total weight.

It is thus concluded that under the temperature/pressure conditions required for high vapor densities, the formation of polyatomic species is not expected to tie up a significant amount of tin atoms which are considered necessary in the proposed pumping scheme which leads to electronically excited SnO*.

2. The composition of germanium vapor in the torr-regime consists essentially of monatomic Ge (98%) and a very small amount of dimer Ge_2 (2%). No higher molecular weight species were observed in the temperature range $1700^{\circ}K - 2000^{\circ}K$.

3. The composition of silicon vapor is somewhat more complex. In the vicinity of $2500^{\circ}K$ where the vapor pressure exceeds one torr, the vapor in addition to Si atoms contains Si_2, Si_3, and Si_4, totalling about 10% of the total.

4. The volatility of tin oxide is higher than that of the tin metal by two orders of magnitude; this is a desirable property in terms of attempting to build a laser on the tin oxide system.

IV. CONCLUSIONS (Cont)

5. The high exothermicity of the Ti/B reaction has been utilized to vaporize tin in relatively large quantities. Several grams of tin can be vaporized over a period of one second by this technique. Favorable conditions for effective vaporization have been identified and a small tube-like generator was built.

6. The limited study of the emission spectra of the $Sn-N_2O$ system suggests that the SnO green system ($a^3\sum^+ \rightarrow X'\sum'$) appears only at low Sn densities as dictated by low temperatures ($1473^{\circ}K-1673^{\circ}K$). In the $1673^{\circ}K-2270^{\circ}K$ range the green system is replaced by the blue $C \rightarrow X'\sum^+$ and $D'\pi \rightarrow X'\sum^+$ SnO systems. Appearance of the upper state Sn lines at 3801 and $4524\overset{\circ}{A}$ at high intensity suggests a non thermal Sn distribution.

7. Based on qualitative observations of the Sn/N_2O system, it can be stated that Sn vapor (in contrast with other metals) burns with difficulty in ambient N_2O and the intensity of green system appears to decrease when the density of the tin vapor increases.

Energy Pooling / Bad News

$$SnO^* + SnO^* \rightarrow SnO + SnO^{**}$$

could this effect and #6 relate to fraction of $Sn(^3\pi_1)$ made by generator?